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(54) Photopolymerizable epoxy resin composition.

(57) There is disclosed a photopolymerizable epoxy resin composition comprising an epoxy resin; and a heteropoly-acid aromatic sulfonium salt or a heteropoly-acid aromatic iodonium salt as a photo-curing catalyst.

The composition of this invention can exhibit the photopolymerization being promptly advanced, the cured product being great in hardness, the corrosive action being weak, and the electrical properties being excellent.

Therefore, an industrial utility of the composition of this invention is highly great.

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Photopolymerizable epoxy resin compositionBACKGROUND OF THE INVENTION

This invention relates to a photopolymerizable epoxy resin composition having a novel composition, more particularly to an epoxy resin composition having good photo-curability, less corrosive properties and excellent electrical characteristics.

In the specifications of U.S. Patents No. 3,205,156 and No. 3,708,296, there are disclosed light-susceptible epoxy resin compositions containing an aryldiazonium salt and an aryldiazonium salt of a halogen-containing complex anion, respectively. These compositions are restricted in their availabilities for reasons of (1) a less thermal stability, (2) spectral responses being limited to an ultraviolet region of spectrum, and (3) the occurrence of pinholes and air bubbles in a cured composition due to the generation of nitrogen during photopolymerization.

Also when oxetane or a mixture of oxetane and an epoxy resin is photopolymerized by the use of aforesaid aryldiazonium salt, the same problem as mentioned above will arise (see the specification of U.S. Patent No. 3,835,003).

Some patents (see specifications of U.S. Patents No. 3,711,390, No. 3,711,931, No. 3,816,278, No. 3,817,850 and No. 3,817,845) disclose methods for stabilizing mixtures of diazonium salts and epoxides. These methods, however, are unsatisfactory for several reasons. For example, with regard to their stability, its good state can merely be retained for so short a period as to be represented by the unit of days, and the addition of a stabilizer, which is a non-reactive material, will contaminate a desired composition, with the consequence that this added material will soften a product thereof and will deteriorate a photo-setting speed.

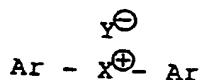
Further, in the specification of U.S. Patent No. 3,450,613, there is disclosed a photopolymerizable epoxy resin composition comprising a reaction product of an epoxy resin prepolymer and an ethylenically unsaturated organic acid, a light-susceptible agent and optionally a poly-functional acid or hydrochloric acid.

The gelation of this composition can be accomplished by the photopolymerization of an ethylenically unsaturated portion in the reaction product when exposed to ultra-violet rays, but for the sake of the complete cure of the composition, it is necessary that an epoxy resin portion of the composition is caused to carry out a curing reaction. For this purpose, it is finally required to give a thermal treatment to the composition. In other words, in order to accomplish the complete polymerization (curing) of this composition, both light and heat are needful. For this reason, applicable fields of the composition are inevitably limited. In addition thereto, this composition has the problems of being sensitive to enzymes and being low in thermal stability.

On the other hand, as photo-setting catalysts for the photopolymerizable epoxy resin composition, complexes

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represented by the following formula are known:



wherein Ar is a phenyl group or the like; X is an iodine atom, sulfur atom diazo group or the like; and Y is BF_4 , PF_6 , AsF_6 , SbF_6 or the like.

- 5 [see, for example, Macromolecules, Vol. 10, p. 1307 (1977); Journal of Radiation Curing, Vol. 5, p. 2 (1978); Journal of Polymer Science, Polymer Chemistry Edition, Vol. 17, p. 2877 (1979); Ibid. Vol. 17, p. 1047 (1979);
10 Journal of Polymer Science, Polymer Letters Edition, Vol. 17, p. 759 (1979); Japanese Provisional Patent Publication No. 65219/1980; U.S. Patent No. 4,069,054; and British Patents No. 1,516,511 and No. 1,518,141.]

However, when the photopolymerization of the epoxy resin is carried out with this photo-setting catalyst, the
15 cured material will be improved in mechanical properties, but on the other hand, if used in the field of electric appliances, the cured material will inevitably
deteriorate in electrical insulating properties and will
corrode peripheral parts, because the added catalyst
20 functions as an ionic impurity.

SUMMARY OF THE INVENTION

An object of this invention is to provide a novel photopolymerizable composition which can overcome the
aforesaid problems inherent in a photopolymerizable epoxy
25 resin composition, has excellent photo-setting properties and a less corrosive action, and permits giving satisfactory electrical properties to a prepared cured material.

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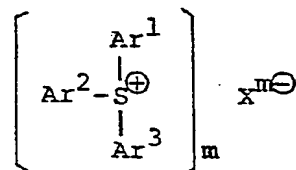
A photopolymerizable epoxy resin composition of this invention is characterized by comprising an epoxy resin and an aromatic sulfonium salt of a heteropoly-acid or an aromatic iodonium salt of a heteropoly-acid.

5 DESCRIPTION OF THE PREFERRED EMBODIMENTS

Examples of the epoxy resins to be used in this invention include a bisphenol A type epoxy resin; a bisphenol F type epoxy resin; a phenol-novolac type epoxy resin; an alicyclic epoxy resin; a heterocyclic ring-containing
 10 epoxy resin such as triglycidyl isocyanurate, hydantoin epoxy, or the like; a hydrogenated bisphenol A type epoxy resin; an aliphatic epoxy resin such as propylene glycol-diglycidyl ether, pentaerythritol-polyglycidyl ether or the like; a glycidyl ester type epoxy resin obtained by
 15 the reaction of an aromatic, aliphatic or alicyclic carboxylic acid with epichlorohydrin; a spiro ring-containing epoxy resin; a glycidyl ether type epoxy resin which is a reaction product of an o-allyl-phenol-novolac compound and epichlorohydrin; a glycidyl ether type epoxy
 20 resin which is a reaction product of a diallyl bisphenol compound, having an allyl group at the o-position of each of the hydroxyl groups in bisphenol A, and epichlorohydrin; etc.

The heteropoly-acid aromatic sulfonium salt to be used in
 25 this invention is one of an essential component as a photopolymerization initiator.

This heteropoly-acid aromatic sulfonium salt is a compound generally represented by the following formula:



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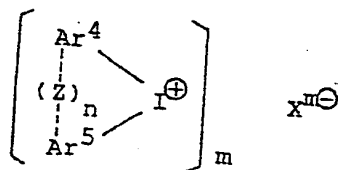
wherein Ar^1 to Ar^3 may be the same or different from each other, and each represents an aromatic group such as a phenyl group or a naphthyl group; or an aromatic group substituted with at least one substituent selected from the group consisting of a halogen atom, an alkyl group, an alkoxy group, an aralkyl group, an aryloxy group, an arylthio group and a nitro group; X^{m-} represents an anion of the heteropoly-acid; and m is an integer of 3 to 5.

Examples of the anions X^{m-} of the heteropoly-acid include a phosphotungstate, a phosphomolybdate, a tungstogermate, a silicotungstate, a silicomolybdate and the like.

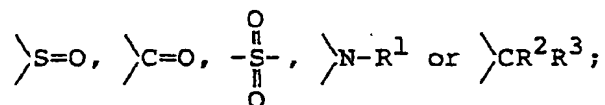
Concrete examples of the heteropoly-acid aromatic sulfonium salt to be used in this invention include triphenylsulfonium phosphomolybdate, triphenylsulfonium phosphotungstate, triphenylsulfonium silicotungstate, tri(methoxyphenyl)sulfonium phosphotungstate, tri(methoxyphenyl)sulfonium silicomolybdate, tri(tert-butylphenyl)sulfonium phosphotungstate, tritolylsulfonium phosphotungstate, tri(2-naphthyl)sulfonium phosphotungstate and the like. Preferably, a phosphotungstate such as triphenylsulfonium phosphotungstate is employed.

The heteropoly-acid aromatic iodonium salt to be used in this invention is another essential component as a photopolymerization initiator.

This heteropoly-acid aromatic iodonium salt is a compound represented by the following formula:



wherein Ar⁴ and Ar⁵ may be the same or different from each other, and each represents a substituted or unsubstituted aromatic group or heterocyclic group each having 6 to 20 carbon atoms; Z represents
5 optional presence of an oxygen atom, a sulfur atom,



where R¹ represents a hydrogen atom, an alkyl group having 1 to 10 carbon atoms or an acyl group having 1 to 5 carbon atoms; and R² and R³ may be the same or different from each other, and
10 each represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms or an alkenyl group having 2 to 4 carbon atoms;
X^{m⊖} represents an anion of the heteropoly-acid; m is an integer of 3 to 5; n is an integer of 0 or 1; and
15 dotted line represents optional presence of bonding when n = 1.

In the formula, examples of the aromatic group or the heterocyclic group represented by Ar⁴ or Ar⁵ include a phenyl group, a thienyl group, a furanyl group, a
20 pyrazolyl group and the like. These aromatic groups may have one or more condensated benzene ring such as a condensated carbon-hydrogen ring, e.g. naphthyl; a sulfur containing condensated heterocyclic ring, e.g. benzo-thienyl, dibenzothienyl, etc.; and an oxygen-containing
25 condensated heterocyclic ring, e.g. benzofuranyl, dibenzofuranyl, etc.

These aromatic groups may optionally be substituted by one or more substituents as described below. Such a substituent include a halogen atom, a nitro group, a
30 hydroxy group, a carboxyl group, an anilino group or N-alkylanilino group, an ester group (e.g. an alkoxycarbonyl such as methoxycarbonyl or ethoxycarbonyl, a phenoxy-

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carbonyl), a sulfo ester group (e.g. an alkoxysulfonyl such as methoxysulfonyl or ethoxysulfonyl, a phenoxy-sulfonyl), an amido group (e.g. an acetamide, a butyl-amide, an ethylsulfonamide), a carbamyl group (e.g. a carbamyl, an N-alkylcarbamyl, an N-phenylcarbamyl), a sulfamyl group (e.g. a sulfamyl, an N-alkylsulfamyl, an N,N-dialkylsulfamyl, an N-phenylsulfamyl), an alkoxy group (e.g. a methoxy, an ethoxy, a butoxy), an aryl group (e.g. a phenyl), an alkyl group (e.g. a methyl, an ethyl, a butyl), an aryloxy group (e.g. a phenoxy), an alkylsulfonyl group (e.g. a methylsulfonyl, an ethyl-sulfonyl), an arylsulfonyl group (e.g. a phenylsulfonyl), a perfluoroalkyl group (e.g. a trifluoromethyl, a perfluoroethyl) and a perfluoroalkylsulfonyl group (e.g. a trifluoromethylsulfonyl, a perfluorobutylsulfonyl).

In the formula, Ar^4 and Ar^5 may be bonded by an oxygen atom, a sulfur atom, $\begin{array}{c} | \\ S=O \\ | \end{array}$, $\begin{array}{c} | \\ C=O \\ | \end{array}$, $\begin{array}{c} | \\ O=S=O \\ | \end{array}$, R^1-N (wherein R^1 represents a hydrogen atom, a lower alkyl group having 1 to 10 carbon atoms, an acyl group such as an acetyl or a benzoyl), or $R^2-\begin{array}{c} | \\ C-R^3 \\ | \end{array}$ (wherein R^2 and R^3 may be the same or different and each represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms or an alkenyl group having 2 to 4 carbon atoms).

In the formula, $X^{m\ominus}$ has the same meaning as defined above.

Concrete examples of the heteropoly-acid aromatic iodonium salt to be used in this invention include diphenyliodonium phosphomolybdate, diphenyliodonium phosphotungstate, di(4-methylphenyl)iodonium phosphosilicotungstate, di(4-heptylphenyl)iodonium tungstogermanate, di(5-nitrophenyl)iodonium phosphotungstate, di(4-chlorophenyl)iodonium silicomolybdate, dinaphthylidonium phosphotungstate, di(4-trifluoromethylphenyl)iodonium

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phosphotungstate, di(2-benzothienyl)iodonium phosphotungstate, di(2-naphthyl)sulfonium phosphotungstate, and the like.

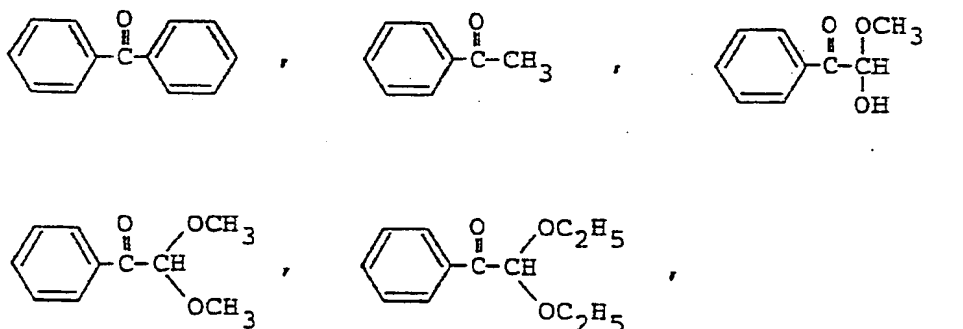
Among them, a diaryliodonium phosphotungstate such as
5 diphenyliodonium phosphotungstate is preferably employed.

These heteropoly-acid aromatic iodonium salt may be prepared by applying the method as disclosed in "Macromolecules, Vol. 10, No. 6, p. 1307 (1977)".

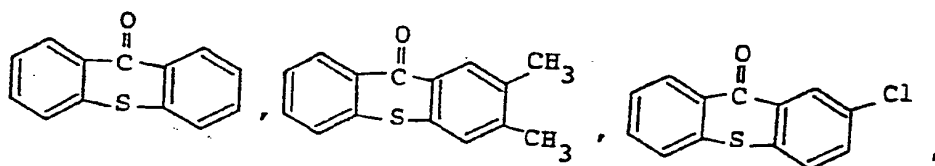
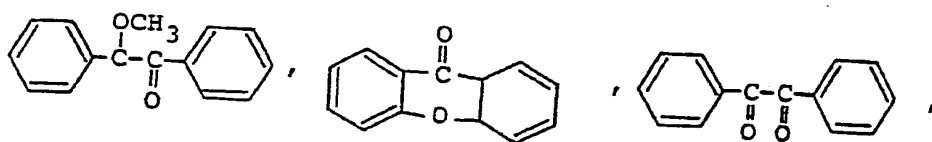
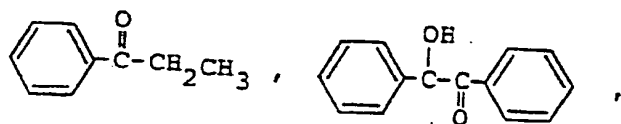
A mixing amount of the heteropoly-acid aromatic sulfonium
10 salt or the heteropoly-acid aromatic iodonium salt is preferably within 0.001 to 10 parts by weight, more preferably within 0.1 to 5 parts by weight based on 100 parts by weight of the epoxy resin. When the amount of the heteropoly-acid aromatic sulfonium salt or the
15 heteropoly-acid aromatic iodonium salt is less than 0.1 parts by weight, the photopolymerization will not make progress to a satisfactory degree; when it is more than 10 parts by weight, there will be induced inconvenient matters such as heightened corrosive properties,
20 increased costs and deteriorated electrical properties.

In this invention, a sensitizer may also be added, if desired.

Concrete examples of the sensitizer include:



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phenanthrene, naphthalene, 2-nitrofluorene, anthracene, benzoquinone, chrycene and the like. These sensitizer may preferably be mixed in an amount of 0.001 to 20 % by weight based on the epoxy resin.

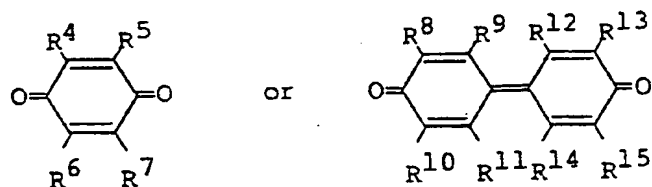
- 5 When preparing the composition of this invention, a phenol compound or an acid anhydride may optionally be added in addition to the above essential two components.

In this invention, a cured product having good properties can be obtained by further adding a quinone derivative.

- 10 The quinone derivative is a component having a function of regenerating the heteropoly-acid which was lowered in acidity due to the reduction by irradiation of ultra-violet light.

- 15 The quinone derivative is a compound having the following formula:

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wherein R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} and R^{15} may be the same or different, and each represents a group selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group, a cyano group and a nitro group; or a pair selected from the group consisting of R^4 and R^5 , R^6 and R^7 , R^8 and R^9 , R^{10} and R^{11} , R^{12} and R^{13} , and R^{14} and R^{15} represents an aromatic condensed ring,

and concrete example thereof include p-benzoquinone, o-benzoquinone, 1,4-naphthoquinone, 2-methyl-1,4-naphthoquinone, 2,3,5,6-tetrachloro-p-benzoquinone, anthraquinone, phenanthrenequinone, 2-methyl-anthraquinone, benzo[*a*]anthraquinone, 1,2-dihydroxyanthraquinone, 4,4'-diphenoquinone, 3,3',5,5'-tetra-tert-butyl-4,4'-diphenoquinone, 3,3',5,5'-tetramethyl-4,4'-diphenoquinone and the like.

A mixing amount of the quinone derivative is preferably within 0.01 to 10 parts by weight based on 100 parts by weight of the epoxy resin. When the amount of the quinone derivative is less than 0.01 part by weight, regeneration of the photopolymerization catalyst will be insufficient; on the contrary, when it exceeds 10 parts by weight, coloring will occur or adhesive property will deteriorate.

The photopolymerizable compositions of this invention can be cured by methods such as room-temperature photo-curing, high-temperature photo-curing, after-cure which is effected after the photo-curing, etc. The wavelength of light necessary for the photo-curing will generally be

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from 180 nm to 600 nm, preferably from 300 nm to 400 nm; the irradiation time will generally be from 0.5 sec. to 10 min., preferably from 1 sec. to 1 min., depending on the epoxy resin composition and the catalyst to be used; and the temperature in case of high-temperature photocuring will generally be from 20 °C to 200 °C, preferably from 60 °C to 100 °C, depending on the epoxy resin composition and the catalyst to be used. Examples of the light source to be used in this invention may include a high-pressure mercury-vapor lamp, a carbon arc lamp, a xenon lamp, an argon glow discharge tube, metal halide lamp and the like. In case of after-cure which is effected after the photo-curing will generally be carried out at 50 °C to 200 °C, preferably at 100 °C to 180 °C, and effected for 1 to 10 hrs., preferably for 2 to 5 hrs., depending on the epoxy resin composition and the catalyst to be used.

The resulting cured material has extremely excellent electrical properties.

As is definite from the foregoing, the composition of this invention can exhibit (1) the photopolymerization being promptly advanced, (2) the cured product being great in hardness, (3) the corrosive action being weak, and (4) the electrical properties being excellent. Therefore, it is fair to say that an industrial utility of the composition of this invention is highly great.

A photopolymerizable composition of this invention will be described in detail as examples.

Examples 1 to 6

As epoxy resins, there were used Epikote 828 (trade name, available from Shell Kagaku K.K., Japan; bisphenol A type epoxy resin; epoxy equivalent: 190 to 210), Epikote 1001

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(trade name, available from Shell Kagaku K.K., Japan; bisphenol A type epoxy resin; epoxy equivalent: 450 to 525; molecular weight: 900) and Epikote 1004 (trade name, available from Shell Kagaku K.K., Japan; bisphenol A type epoxy resin; epoxy equivalent: 900 to 1000; molecular weight: 1400), and as photopolymerization initiators, there were used triphenylsulfonium phosphotungstate, tri-(methylphenyl)sulfonium phosphotungstate and triphenylsulfonium phosphomolybdate.

- 10 Each of these materials was uniformly mixed in compounding proportions (which were represented with "parts by weight") shown in Table 1 below in order to prepare epoxy resin compositions of this invention.

Each of these compositions was applied onto aluminum plates, and was then introduced into an ultraviolet irradiation photo-curing device in which an intensity of the irradiation was adjusted to 80 W/cm, and photo-curing was carried out for a predetermined period of time. The resultant coating films on the plates were tested for pencil hardness and dielectric loss tangent value ($\tan \delta$: %) at 180 °C. The obtained results are shown in Table 1 all together.

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Table 1

	Example					
	1	2	3	4	5	6
<u>Epoxy resin</u>						
Epikote 828	80	80	70	70	50	80
Epikote 1001	20		30		20	20
Epikote 1004		20		30		
<u>Heteropoly-acid aromatic sulfonium salt</u>						
Triphenylsulfonium phosphotungstate	4					
Tri(methylphenyl)sulfonium phosphotungstate		4		4	4	
Triphenylsulfonium phosphomolybdate			4			
Tri(2-naphthyl)sulfonium phosphotungstate						3
<u>Measured value</u>						
Tan δ (%)	3.2	3.1	3.5	3.2	4.0	3.9
Pencil hardness	2H	3H	2H	3H	3H	3H
Curing time (sec.)	30	30	30	45	45	30
Thickness of coating film (μ m)	20	20	15	15	20	10

Examples 7 to 14

As epoxy resins, there were used Epikote 828 (trade name, available from Shell Kagaku K.K., Japan; bisphenol A type epoxy resin; epoxy equivalent: 190 to 210), Epikote 1001 (trade name, available from Shell Kagaku K.K., Japan; bisphenol A type epoxy resin; epoxy equivalent: 450 to 525; molecular weight: 900) and Epikote 1004 (trade name, available from Shell Kagaku K.K., Japan; bisphenol A type epoxy resin; epoxy equivalent: 900 to 1000; molecular weight: 1400), as heteropoly-acid aromatic iodonium salts, there were used diphenyliodonium phosphotungstate,

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di(methylphenyl)iodonium phosphotungstate and diphenyl-
iodonium phosphomolybdate, and as the sensitizers, there
were used dimethylthioxanthone and benzophenone.

5 Each of these materials was uniformly mixed in
compounding proportions (which were represented with
"parts by weight") shown in Table 2 below in order to
prepare epoxy resin compositions of this invention.

10 Each of these compositions was applied onto aluminum
plates, and was then introduced into an ultraviolet
irradiation photo-curing device in which an intensity of
the irradiation was adjusted to 80 W/cm, and photo-curing
was carried out for a predetermined period of time. The
resultant coating films on the plates were tested for
pencil hardness and dielectric loss tangent value ($\tan \delta$:
15 %) at 180 °C. The obtained results are shown in Table 2
all together.

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Table 2

Epoxy resin	7	8	9	10	11	12	13	14	Comparative example 1
Epikote 828	100	80	80	60	60	50	70	80	100
Epikote 1001	-	20	-	40	20	50	20	20	-
Epikote 1004	-	-	20	-	20	-	10	-	-
Heteropoly-acid aromatic iodonium salt	-	-	-	-	-	-	-	-	-
Diphenyliodonium phosphomolybdate	2	-	-	2	-	-	2	-	2
Diphenyliodonium phosphotungstate	-	2	-	-	2	-	-	-	-
Di(methylphenyl)iodonium phosphomolybdate	-	-	2	-	-	2	-	-	-
Di(2-naphthyl)iodonium phosphotungstate	-	-	-	-	-	-	-	-	-
Sensitizer	-	-	-	-	-	-	-	2	-
Dimethylthioxanthone	1	1	1	-	-	1	-	1	-
Benzophenone	-	-	-	1	1	-	1	-	-
Measured value	-	-	-	-	-	-	-	-	-
Curing time (sec.)	30	30	50	30	30	60	60	40	60
Tan δ (%)	2.5	3.0	2.7	2.9	2.1	3.4	3.5	2.9	3.1
Pencil hardness	4H	4H	5H	4H	4H	4H	4H	3H	3H
Thickness of coating film (μm)	20	10	15	15	15	10	10	10	20

Examples 16 to 20

As epoxy resins, there were used ERL 4221 (trade name, available from Union Carbide Co.; 3',4'-epoxy-cyclohexyl-methyl-3,4-epoxy-cyclohexanecarboxylate), Epikote 828 (trade name, available from Shell Kagaku K.K., Japan; bisphenol A type epoxy resin; epoxy equivalent: 190 to 210), Epikote 1001 (trade name, available from Shell Kagaku K.K., Japan; bisphenol A type epoxy resin; epoxy equivalent: 450 to 525; molecular weight: 900), Epikote 1004 (trade name, available from Shell Kagaku K.K., Japan; bisphenol A type epoxy resin; epoxy equivalent: 900 to 1000; molecular weight: 1400), ERL 4206 (trade name, available from Union Carbide Co.; vinylcyclohexene-dioxide) and CY 175 (trade name, available from Chiba Geigy A.G.; alicyclic epoxide), as heteropoly-acid aromatic iodonium salts, there were used diphenyliodonium phosphotungstate, di(methylphenyl)iodonium phosphomolybdate and diphenyliodonium phosphomolybdate, and as quinone derivatives, there were used p-benzoquinone and 1,4-naphthoquinone.

Each of these materials was uniformly mixed in compounding proportions (which were represented with "parts by weight") shown in Table 3 below in order to prepare epoxy resin compositions of this invention.

- 25 Each of these compositions was applied onto aluminum plates, and was then introduced into an ultraviolet irradiation photo-curing device in which an intensity of the irradiation was adjusted to 80 W/cm, and photo-curing was carried out for a predetermined period of time.
- 30 The resultant coating films on the plates were tested for pencil hardness and dielectric loss tangent value ($\tan \delta$: %) at 180 °C. The obtained results are shown in Table 3 all together.

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Table 3

Epoxy resin	Example							Comparative example	
	15	16	17	18	19	20	21	2	3
Epikote 828	-	-	30	20	50	-	-	-	-
Epikote 1001	-	-	20	-	20	30	-	-	-
Epikote 1004	-	-	-	20	-	-	-	-	-
ERL 4221	50	50	50	50	30	50	50	50	50
ERL 4206	50	-	-	-	-	20	50	-	-
CY 175	-	50	-	10	-	-	-	-	50
Heteropoly-acid aromatic iodonium salt	-	-	-	-	-	-	-	-	-
Diphenyliodonium phosphomolybdate	-	-	5	-	-	-	-	-	-
Diphenyliodonium phosphotungstate	4	-	-	4	5	5	4	-	-
Di(methylphenyl)iodonium phosphomolybdate	-	4	-	-	-	-	-	-	4
Quinone derivative	-	-	-	-	-	-	-	-	-
p-Benzoquinone	2	2	-	1	1	2	-	-	-
1,4-Naphthoquinone	-	-	2	-	-	-	-	-	-
Measured value	-	-	-	-	-	-	-	-	-
Tan δ (%) at 180 °C	3.6	5.2	4.5	2.9	3.0	3.5	3.3	5.0	-
Pencil hardness	5H	H	2H	3H	3H	3H	3H	H	-
Curing time (sec.)	5	2	5	3	5	5	25	15	-
Thickness of coating film (μ m)	20	20	10	20	10	20	20	20	20

Example 21

Corrosivity to iron of the epoxy resin compositions of this invention was measured with the Coulstatt method.

A epoxy resin (Celloxide 2021; trade name, available from
5 Daisel K. K., alicyclic epoxy resin) which was photo-
cured (80 W/cm, at a distance of 15 cm for 1 minute) with
a catalyst (tri(methoxyphenyl)sulfonium silicotungstate:
1 phr) was crushed into powder having particle size
between 100 meshes to 300 meshes. After 50 g of the thus
10 prepared powders were placed in a 500 cc of distilled
water and refluxed for an hour, the mixture was filtrated
to obtain an aqueous filtrate. An iron plate which was
covered with Capton tape (trade name; available from
Teraoka Seisakusho Co.) leaving a not covered area of 2
15 cm x 1, was inserted into the filtrated aqueous solution
to measure the corrosive speed.

On the other hand, the same procedures were repeated
except that the catalyst was replaced with UVE 1014
(aromatic sulfonium hexafluoroantimonate, available from
20 GE) to prepare Comparative sample 4.

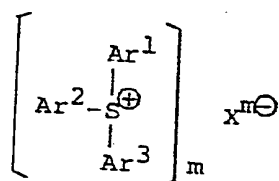
As the results, in the case of epoxy resin composition of
this invention, an initial corrosive speed was 9 mg/day/
(dm)² whereas the Comparative sample 4 being 100 mg/day/
(dm)². Therefore, it is confirmed that the catalyst
25 system of this invention is smaller in corrosive speed
than that of the Comparative sample.

As is definite from the foregoing, the composition of
this invention can exhibit the effects of the photopoly-
merization being promptly advanced; the cured product
30 being great in hardness; and the electrical properties
being excellent. Therefore, it is fair to say that an
industrial utility thereof is highly great.

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Claims:

1. A photopolymerizable epoxy resin composition comprising an epoxy resin; and a heteropoly-acid aromatic sulfonium salt or a heteropoly-acid aromatic iodonium salt.
2. The photopolymerizable epoxy resin composition according to Claim 1, wherein the epoxy resin being an epoxy resin selected from the group consisting of a bisphenol A type epoxy resin, a bisphenol F type epoxy resin, a phenol-novolac type epoxy resin, an alicyclic epoxy resin, a heterocyclic ring-containing epoxy resin, a hydrogenated bisphenol A type epoxy resin, an aliphatic epoxy resin, a glycidyl ester type epoxy resin, a spiro ring-containing epoxy resin and a glycidyl ether type epoxy resin.
3. The photopolymerizable epoxy resin composition according to Claim 1, wherein the heteropoly-acid aromatic sulfonium salt being a compound represented by the formula:



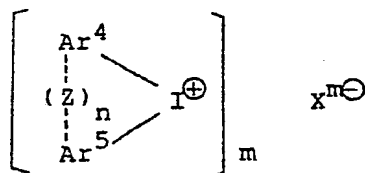
wherein Ar^1 to Ar^3 may be the same or different from each other, and each represents an aromatic group, or an aromatic group substituted with at least one substituent selected from the group consisting of a halogen atom, an alkyl group, an alkoxy group, an aralkyl group, an aryloxy group, an arylthio group and a nitro group; $\text{X}^{\text{m}\ominus}$ represents an anion of a heteropoly-acid; and m is an integer of 3 to 5.

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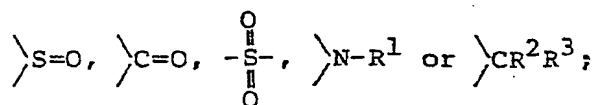
4. The photopolymerizable epoxy resin composition according to Claim 3, wherein the $X^{m\ominus}$ being an anion selected from the group consisting of a phosphotungstate, a phosphomolybdate, a tungstogermanate, a silicotungstate and a silicomolybdate.

5. The photopolymerizable epoxy resin composition according to Claim 3, wherein the heteropoly-acid aromatic sulfonium salt being a compound selected from the group consisting of triphenylsulfonium phosphomolybdate, triphenylsulfonium phosphotungstate, triphenylsulfonium silicotungstate, tri(methoxyphenyl)sulfonium phosphotungstate, tri(methoxyphenyl)sulfonium silicomolybdate, tri(tert-butylphenyl)sulfonium phosphotungstate, tritolylsulfonium phosphotungstate and tri(2-naphthyl)sulfonium phosphotungstate.

6. The photopolymerizable epoxy resin composition according to Claim 1, wherein the heteropoly-acid aromatic iodonium salt being a compound represented by the formula:



wherein Ar^4 and Ar^5 may be the same or different from each other, and each represents a substituted or unsubstituted aromatic group or heterocyclic group each having 6 to 20 carbon atoms; Z represents optional presence of an oxygen atom, a sulfur atom,



where R^1 represents a hydrogen atom, an alkyl group having 1 to 10 carbon atoms or an acyl group having 1 to 5 carbon atoms; and R^2 and R^3

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may be the same or different from each other, and each represents a hydrogen atom, an alkyl group having 1 to 4 carbon atoms or an alkenyl group having 2 to 4 carbon atoms;
5 X^{m-} represents an anion of the heteropoly-acid; m is an integer of 3 to 5; n is an integer of 0 or 1; and dotted line represents optional presence of bonding when $n = 1$.

7. The photopolymerizable epoxy resin composition
10 according to Claim 6, wherein the X^{m-} being an anion selected from the group consisting of a phosphotungstate, a phosphomolybdate, a tungstogermanate, a silicotungstate and a silicomolybdate.

8. The photopolymerizable epoxy resin composition
15 according to Claim 6, wherein the heteropoly-acid aromatic iodonium salt being a compound selected from the group consisting of diphenyliodonium phosphomolybdate, diphenyliodonium phosphotungstate, di(4-methylphenyl)-
20 iodonium phosphosilicotungstate, di(4-heptylphenyl)iodonium tungstogermanate, di(5-nitrophenyl)iodonium phosphotungstate, di(4-chlorophenyl)iodonium silicomolybdate, dinaphthyl
25 iodonium phosphotungstate, di(4-trifluoromethylphenyl)iodonium phosphotungstate, di(2-benzothienyl)iodonium phosphotungstate and di(2-naphthyl)sulfonium phosphotungstate.

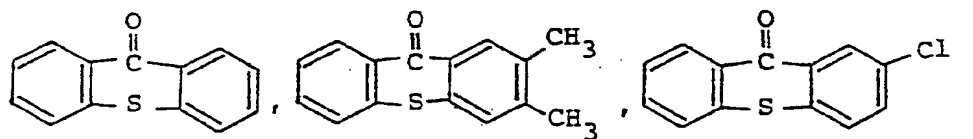
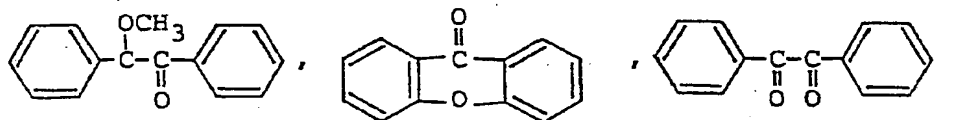
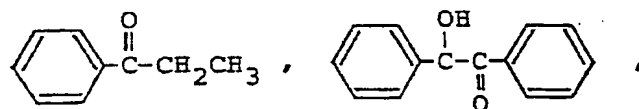
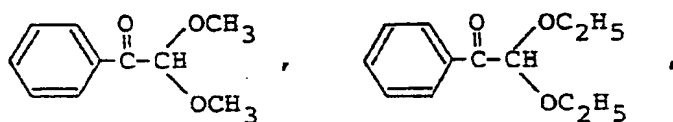
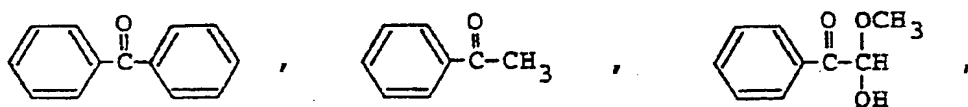
9. The photopolymerizable epoxy resin composition
according to Claim 1, wherein the amount of the heteropoly-acid aromatic sulfonium salt or the heteropoly-acid
30 aromatic iodonium salt being within the range of 0.001 to 10 parts by weight based on the 100 parts by weight of the epoxy resin.

10. The photopolymerizable epoxy resin composition
according to Claim 9, wherein the amount of the hetero-

poly-acid aromatic sulfonium salt or the heteropoly-acid aromatic iodonium salt being within the range of 0.1 to 5 parts by weight based on the 100 parts by weight of the epoxy resin.

5 11. The photopolymerizable epoxy resin composition according to Claim 1, the composition further comprises a sensitizer.

10 12. The photopolymerizable epoxy resin composition according to Claim 11, the sensitizer being a compound selected from the group consisting of



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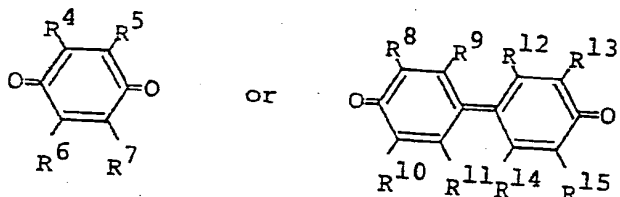
phenanthrene, naphthalene, 2-nitrofluorene, anthracene, benzoquinone and chrycene.

13. The photopolymerizable epoxy resin composition according to Claim 11, the amount of the sensitizer being within the range of 0.001 to 20 % by weight based on the epoxy resin.

14. The photopolymerizable epoxy resin composition according to Claim 11, wherein the composition comprises an epoxy resin; a heteropoly-acid aromatic iodonium salt; and a sensitizer.

15. The photopolymerizable epoxy resin composition according to Claim 1, the composition further comprises a quinone derivative.

16. The photopolymerizable epoxy resin composition according to Claim 15, the quinone derivative being a compound represented by the formula:



wherein R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴ and R¹⁵ may be the same or different, and each represents a group selected from the group consisting of a hydrogen atom, a halogen atom, an alkyl group, a cyano group and a nitro group; or a pair selected from the group consisting of R⁴ and R⁵, R⁶ and R⁷, R⁸ and R⁹, R¹⁰ and R¹¹, R¹² and R¹³, and R¹⁴ and R¹⁵ represents an aromatic condensed ring.

17. The photopolymerizable epoxy resin composition according to Claim 15, the quinone derivative being a

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5 compound selected from the group consisting of p-benzoquinone, o-benzoquinone, 1,4-naphthoquinone, 2-methyl-1,4-naphthoquinone, 2,3,5,6-tetrachloro-p-benzoquinone, anthraquinone, phenanthrenequinone, 2-methyl-anthraquinone, benzo[a]anthraquinone, 1,2-dihydroxyanthraquinone, 4,4'-diphenoquinone, 3,3',5,5'-tetra-tert-butyl-4,4'-diphenoquinone and 3,3',5,5'-tetramethyl-4,4'-diphenoquinone.

10 18. The photopolymerizable epoxy resin composition according to Claim 15, the amount of the quinone derivative being within the range of 0.01 to 10 parts by weight based on the 100 parts by weight of the epoxy resin.

15 19. The photopolymerizable epoxy resin composition according to Claim 15, wherein the composition comprises an epoxy resin; a heteropoly-acid aromatic iodonium salt; and a quinone derivative.



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Photopolymerizable epoxy resin composition.

There is disclosed a photopolymerizable epoxy resin composition comprising a epoxy resin; and a heteropoly-acid aromatic sulfonium salt or a heteropoly-acid aromatic iodonium salt as a photo-curing catalyst.

The composition of this invention can exhibit the photopolymerization being promptly advanced, the cured product being great in hardness, the corrosive action being weak, and the electrical properties being excellent.

Therefore, an industrial utility of the composition of this invention is highly great.

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EUROPEAN SEARCH REPORT

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EP 84 11 1648

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	EP-A-0 011 918 (ICI) * claims 1,2,4-6; page 10, lines 7-21 *	1,2,9-14	C 08 G 59/68 G 03 C 1/68
A		3-8,15-19	
X	GB-A-2 034 317 (ICI) * claims 1-3,5; page 3, lines 77-100 *	1,2,9-14	
A		3-8,15-19	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 G G 03 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-01-1985	
		Examiner DEPIJPER R.D.C.	

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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